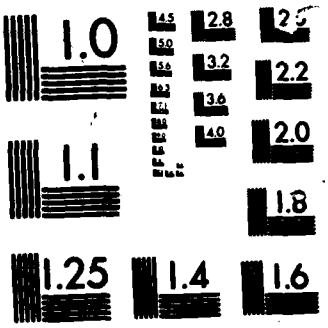
AD-A166 661 DIRECTED SYNTHESIS/FABRICATION AND SURFACE MODIFICATION 1/1
OF IR WINDOW MATE.. (U) ROCKWELL INTERNATIONAL THOUSAND
OAKS CA SCIENCE CENTER A HARKER ET AL. APR 86
UNCLASSIFIED SC5422.AR N00014-85-C-0140 F/G 20/6 NL



MICROCOPY CHART

(12)

SC5422.AR

Copy No. 2

SC5422.AR

DIRECTED SYNTHESIS/FABRICATION AND SURFACE MODIFICATION OF IR WINDOW MATERIALS FOR THE 8-14 MICRON REGION

ANNUAL REPORT NO. 1 FOR THE PERIOD March 1, 1985 through February 28, 1986

CONTRACT NO. N00014-85-C-0140

Prepared for

Engineering Sciences Program
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

A. Harker
P. Morgan
Principal Investigators

APRIL 1986

Approved for public release; distribution unlimited

THIS WORK WAS SUPPORTED IN PART BY THE OFFICE OF NAVAL RESEARCH

Rockwell International
Science Center

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

AD-A166 661

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) SC5422.AR	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION Rockwell International Science Center 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
6c. ADDRESS (City, State and ZIP Code) 1049 Camino Dos Rios Thousand Oaks, CA 91360	7b. ADDRESS (City, State and ZIP Code)
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research Engineering Sciences Program 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract No. N00014-85-C-0140
8c. ADDRESS (City, State and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000	10. SOURCE OF FUNDING NOS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT NO
11. TITLE (Include Security Classification) DIRECTED SYNTHESIS/ FABRICATION AND SURFACE MODIFICATION OF IR WINDOW MATERIALS FOR THE 8-14 MICRON REGION. (U)	
12. PERSONAL AUTHOR(S) Harker, Alan and Morgan, Peter	
13a. TYPE OF REPORT Annual Report No. 1 13b. TIME COVERED FROM 03/01/85 TO 02/28/86	14. DATE OF REPORT (Yr., Mo., Day) 1986 APRIL 15. PAGE COUNT 10
16. SUPPLEMENTARY NOTATION Results of current work will be reported at the SPIE 30th Annual International Technical Symposium, San Diego, California, August 17-22, 1986.	
17. COSATI CODES FIELD / GROUP / SUB. GR.	18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Infrared, transmitting, chalcogenides, thin films.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Nearly monosize particles of pure $NaLaS_2$ have been made by a sulfide fused salt technique. Such particles promise easier compaction and HIPing to highly dense IR window material.

The increased fracture toughness of glass substrates due to the addition of a thin compressive overlayer has been measured. The fracture toughness appears to increase linearly with the total film stress and is independent of the film thickness necessary to provide that stress.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☒ DTIC USERS ☐	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE NUMBER (Include Area Code) 22c. OFFICE SYMBOL

DD FORM 1473, 83 APR EDITION OF 1 JAN 73 IS OBSOLETE.

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

SC5422.AR

TASK I - THE PRODUCTION OF PURE, NEARLY MONOSIZED, PARTICULATE $NaLaS_2$

P.E.D. Morgan

INTRODUCTION

New materials with high transmittance in the 8 - 14 μ IR region and with high strength and thermal shock resistance are desired. In general, the first requirement needs materials with high band gaps to avoid electronic absorption effects and weak bonding with heavier atoms. The other requirements are satisfied by strong bonding and are therefore basically incompatible with the first. Two types of compromise have been attempted. In one, low coordinations with relatively strong covalent bonding such as for ZnS and $ZnSiP_2$[1] do not quite give the desired long wavelength transmittance but do have better thermal shock resitance. The other, typified by the prescient choice of $CaLa_2S_4$,[2-8] is based on the use of many weaker ionic bonds with high coordinate cations and anions. In the latter case thermal shock resistance has been unsatisfactory (at least with the large grain size material), although the long wavelength properties are extremely promising, while still unoptimized.

Our work recognizes the need to produce fine grained ceramic with grain size of less than ~ 5 μ, whose toughness and thermal shock resistance should be superior without degrading the transmittance. To achieve this using the new ceramic paradigm we need < 1 μ uniform particles of the material and we probably must hot-isopress (HIP) the well compacted particles at temperatures preferably $< \sim 1000°C$.

With this in mind, we used $CaLa_2S_4$ as a prototype to test fused salt techniques[9-11] to attain useful results quickly. Later we anticipated expanding the basic technique to whatever ceramic optical material(s) were the best candidate(s).

Experimental and Results

A series of runs was initiated to determine conditions for precipitation and recrystallizing $CaLa_2S_4$ from a Na-Ca-La-S-Cl eutectic melt. Na_2S itself melts at 1175°C and NaCl at 801°C; the eutectic in this system has not been determined as far as we know but the similar case of Na_2S-Na_2CO_3(MP 856°C) has a eutectic at 755°C. It is reasonable to assume a eutectic at < ~ 750°C for the Na_2S-NaCl system. The reaction:

$$CaCl_2 + 2LaCl_3 + 4Na_2S + \text{excess } Na_2S \downarrow$$

$$CaLa_2S_4 + 8NaCl + \text{excess } Na_2S$$

was tried with varying amounts of Ca, La and Na salts weighed out and mixed in a dry box, and fired in a 100% H_2S atmosphere in quartz glass boats in an alumina tube muffle furnace to 800 - 900°C. Slight melting was obvious at ~ 800°C and was pronounced at 900°C. The melts were initially extracted with cold water in which the basic Na_2S-NaCl eutectic is easily soluble and the remnant powder rinsed with acetone and air dried. XRD analysis showed the presence of no $CaLa_2S_4$ but the obvious presence of recently discovered rock salt structure $NaLaS_2$[12] and La_2O_2S contaminant. XRD analysis on the melts, before water extraction, indicated that La_2O_2S was already present and was not a decomposition product of water reactions. Many runs, changing the relative amounts of Ca, La, Na, showed no sign of giving more than traces of $CaLa_2S_4$, but always $NaLaS_2$ was a major component. The by-product La_2O_2S, a sign of contaminant oxygen, was greatly reduced but not eliminated by long slow heat-ups with excess H_2S.

The greater ease of formation of $NaLaS_2$ and the fact that it survived the water washes (and even boiling water for 30 minutes) suggested that it is a more stable compound (i.e., more negative ΔG) than $CaLa_2S_4$ and might be a worthy candidate, at the least for testing out the approach, and at best a real IR candidate. Having a 6:6:6 somewhat ionic coordination, it is a compromise between the types discussed earlier.

For the next tests the almost irreducibly simple reaction:

$$4Na_2S + LaCl_3 \xrightarrow{H_2S} NaLaS_2 + \underbrace{2Na_2S + 3NaCl}_{\text{eutectic liquid}}$$

was tried. Approximately 90% pure $NaLaS_2$ with ~ 10% La_2O_2S was always produced; changes in the ratio of Na:La or extra times in H_2S did not seem to improve the purity. Indeed with large excess of Na_2S, an unknown compound, which we suspect could be something like Na_5LaS_4, and which is unstable with water, appeared also.

The nagging problem of by-product La_2O_2S was solved by replacing the H_2S stream with argon plus CS_2. Argon was merely bubbled through CS_2 liquid in a glass jar before passing over the mixtures throughout the heating and cooling. It was reasoned that carbon might be formed but that if this occurred then the carbon would form a removable layer on top of the melt. In fact carbon was not seen and the La_2O_2S contaminant was removed. Substantially pure $NaLaS_2$ was easily produced.

After extraction with water, no La_2O_2S was seen by XRD, but in future work the eutectic melt will be dissolved by soxhleting with (m)ethanol or THF. SEM-pictures (Fig. 1) of the product indicate that indeed we can produce narrow size distributions of $NaLaS_2$, resulting from the Ostwald ripening phenomenon in the melt. The particles may be showing some incipient cubic faceting and perhaps some superficial decomposition which should be eliminated by the organic extractions.

CONCLUSION

Fused salts with sulfide components seem to be suited for the production of narrow size distribution chalcogenides for IR window and other applications.

SC36382

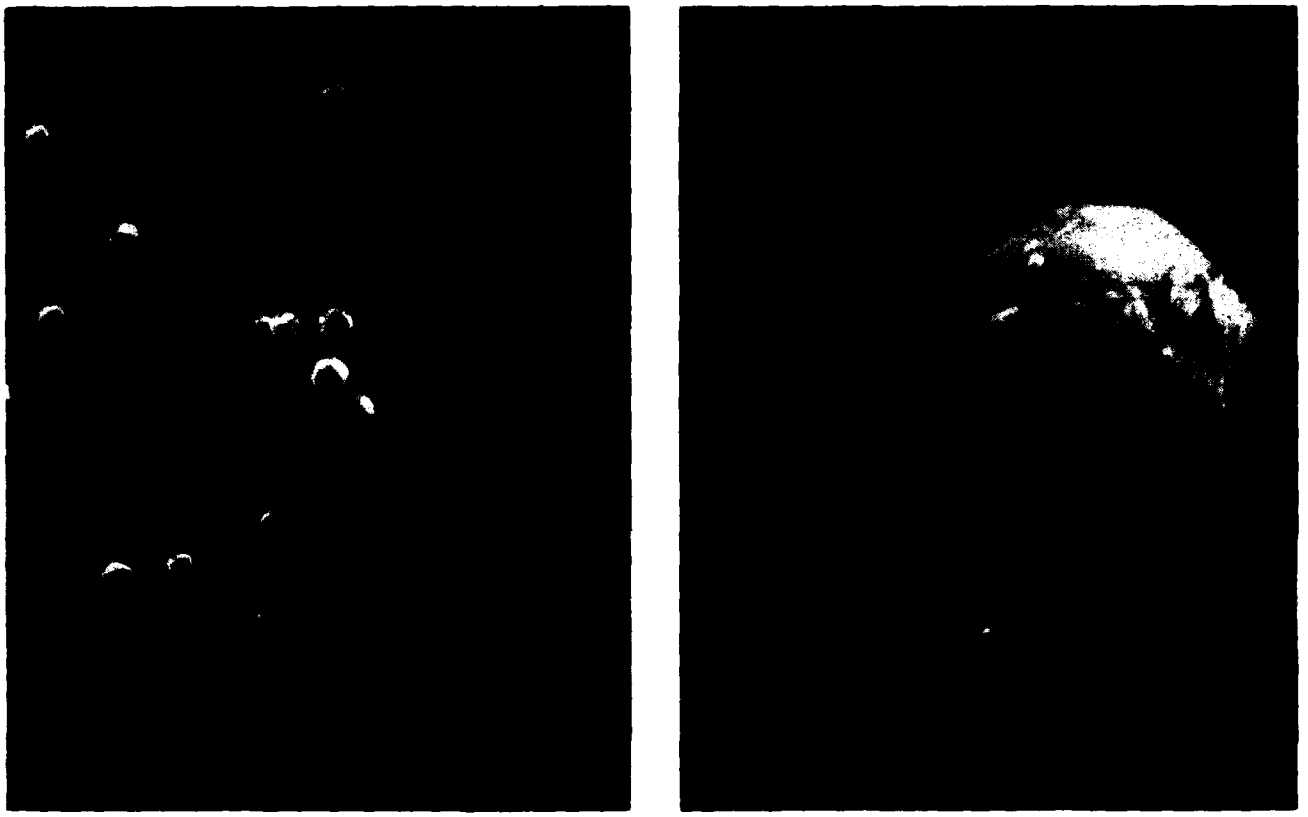


Fig. 1 SEM of particles of $NaLaS_2$.

TASK II - COMPRESSIVE THIN FILMS FOR INCREASED FRACTURE TOUGHNESS

P.H. Kobrin and A.B. Harker

Work on Task 2 has focussed on determining the effects of compressive surface layers on the measured fracture toughness of the bulk substrate. In the initial experiments single layers of Si_3N_4, AlN, and Al_2O_3 were deposited onto glass substrates to determine if a measurable effect upon fracture toughness could be obtained. These tests were designed as a proof of principle as the substrate and film materials are not candidates for LWIR applications, and were selected for their ready availability and the fact that glass gives reproducible measurements of indent hardness and fracture toughness. The Vickers indent method was used since its application to fracture toughness and hardness determination has been well studied.[13] In addition the compressive stress of the films was independently measured using a sensitive bending plate technique with capacitive detection.[14] The goal is to have a model, perhaps empirical, that would relate the increased fracture toughness of a given substrate from a thin film of a given stress and thickness.

Single compressive layers of Si_3N_4, Al_2O_3, and AlN were deposited onto room temperature glass substrates to thicknesses of 500 - 10,000A by reactive ion beam deposition.

With an uncoated substrate, there is a 1-2 decade range of loadings over which the Vickers indentation technique can be expected to yield a good measure of the materials fracture toughness, K. This range varies with different materials as does the range of crack lengths. However, within this useful range, the measured fracture toughness remains relatively constant and is in good agreement with other bulk fracture toughness tests.

With the addition of a thin compressive overlayer, the situation changes. On glass, these < 1 μm thick films are considerably thinner than the penetration depth of the indenter (10-20 μm) or the length of the radial cracks (<80 μm). However, the measured fracture toughness becomes a decreasing function of indenter load, that asymptotically approaches the bulk fracture tough-

ness. The onset of cracking, the minimum load necessary to produce an observable radial crack, also increases dramatically. Thus the compressive film has a proportionally larger effect on the smaller indents.

The results of the fracture toughness measurements on glass are shown in Fig. 2. It can be seen that the increased fracture toughness, taken to be the 1.0 kg-load intercept, increases linearly with film thickness. In addition the slopes are in the order AlN > Si_3N_4 > Al_2O_3.

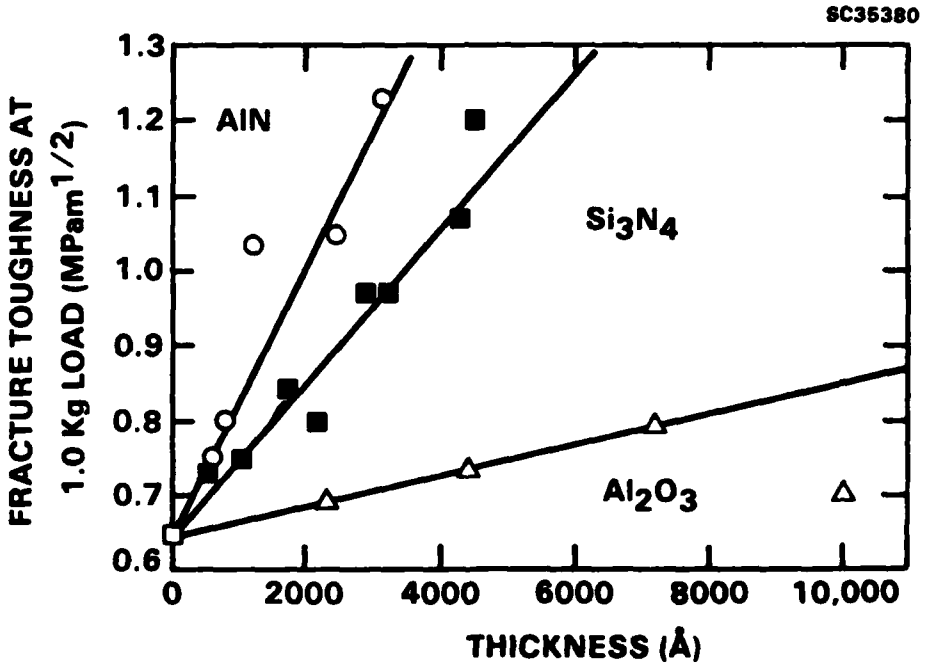


Fig. 2 Increased toughness of glass with films.

Stress measurements made with the bending plate technique gave values of 15 x 10^9 dyne/cm^2 for Si_3N_4 and 2 x 10^9 dyne/cm^2 for Al_2O_3. An example is shown in Fig. 3. The AlN stress measurements proved to be erratic due to oxygen contamination. Comparing results we find that the Si_3N_4 films have 6.5 to 7.5 times more stress than the Al_2O_3 films while the fracture toughness of the Si_3N_4 coated glass increases 5 to 6 times faster with thickness.

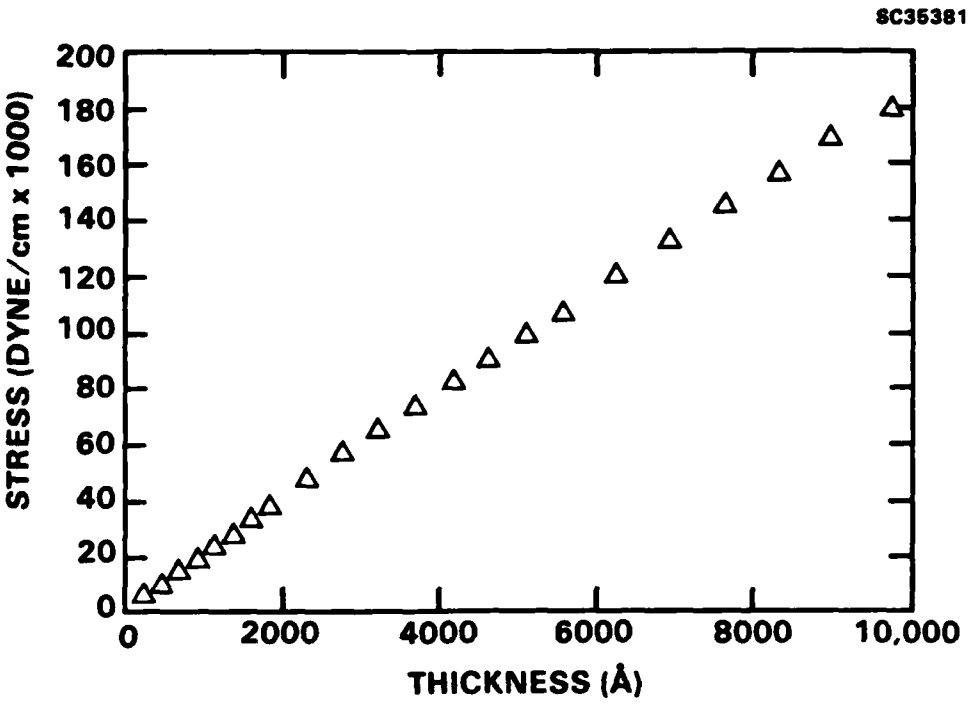


Fig. 3 Stress induced by an ion beam sputtered Al_2O_3 coating.

Thus the fracture toughness appears to increase linearly with the total film stress but is independent of the film thickness necessary to provide that stress. This is in disagreement with the fracture mechanics based model of Lawn and Fuller[15] which has been used to model the decreased fracture toughness of ion irradiated glass. In that model the change in fracture toughness is proportional to the total stress divided by the square root of the layer thickness.

Attempts to extend these studies to spectroscopic grade ZnS (Cleartrans) which is a LWIR material proved futile as the indentation technique does not work well with the size grains present in the Cleartrans. Further studies on the smaller grained, yellow ZnS are therefore planned.

Results of current work will be reported at the SPIE 30th Annual International Technical Symposium, San Diego, California, August 17-22, 1986.

REFERENCES

1. G.Q. Yao, H.S. Shen, R. Kershaw, K. Dwight and A. Wold, "Preparation and Characterization of $ZnSiP_2$ and $ZnGeP_2$ Single Crystals," Tech Rept #1, Office of Naval Research Contract N00014-85-K-0177 (1986).

2. P.L. Provenzano, S.I. Boldish and W.B. White, "Vibrational Spectra of Ternary Sulfides with the Th_3P_4 Structure," Mat. Res. Bull. 12, 936-946 (1977).

3. W.B. White, D. Chess, C.A. Chess and J.V. Biggers, "$CaLa_2S_4$: Ceramic Window Material for the 8 to 14 μm Region," SPIE 297, 38-43 (1981).

4. D.L. Chess, C.A. Chess, J.V. Biggers and W.B. White, "Processings Ternary Sulfide Ceramics: Powder Preparation Sintering, and Hot-Pressing," J. Am. Ceram. Soc. 66, 18-22 (1983).

5. O. Schevciw and W.B. White, "The Optical Absorption Edge of Rare Sesquisulfides and Alkaline Earth - Rare Earth Sulfides," Mat. Res. Bull. 18, 1059-1068 (1983).

6. G.J. McCarthy, J.J. Rhyne and H.B. Silber, "Vibration Spectra of Ternary Rare Earth Sulfides with $CaFe_2O_4$, Yb_3S_4, MnY_2S_4 and $ZnGa_2S_4$ Type Structures," The Rare Earths in Modern Science & Technology 2, 451-456 (1980).

7. P.J. Walker and R.C.C. Ward, "The Preparation of Some Ternary Sulphides MR_2S_4 (M = Ca, Cd: R = La,Sm,Er) and the Melt Growth of $CaLa_2S_4$," Mat. Res. Bull. 19, 717-725 (1984).

8. K.J. Saunders and R.L. Gentilman, "Fabrication Studies of Ternary Rare Earth Sulfides for Infrared Applications," Final Tech. Rept., Office of Naval Research Contract No. N00014-82-C-0413 (1984).

9. D.G. Wickham, "The Preparation of Ferrites With the Aid of Fused Salts," Ferrites 105-7, Proc. Int. Conf. Kyoto, Japan (1970).

10. C.C. Hsu, "Preliminary Results of In Situ Al_2S_3 Preparation in $MgCl_2$-NaCl-KCl Eutectic Melt," J. Electrochem. Soc. 131, 1632-1634 (1984).

11. H.J. Scheel, "Crystallization of Sulfides from Alkali Polysulfide Fluxes," J. Crystal Growth 24/25, 669-673 (1974).

12. M. Sato, G. Adachi and J. Shiokawa, "Preparation and Structure of Sodium Rare-Earth Sulfides, $NaLnS_2$ (Ln; Rare Earth Elements)," Mat. Res. Bull. 19, 215-1220 (1984).

13. G.R. Anstis, P. Chantikul, B.R. Lawn, and D.B. Marshall, "A Critical Evaluation of Indentation Techniques for Measuring Fracture Toughness: I, Direct Cracks Measurements," J. Am. Ceram. Soc. 64, 533-538 (1981).

14. M. Laugier, "Intrinsic Stress in Thin Films of Ag, Al, ZnS and LiF," J. Mat. Sci. 15, 1147-1152 (1980).

15. B.R. Lawn and E.R. Fuller, "Measurement of Thin-Layer Surface Stresses by Indentation Fracture," J. Mat. Sci. 19, 4061-4067 (1984).

END

FILMED

5-86

DTIC